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# Factors Affecting the Stability of Emulsions Stabilised by Biopolymers

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#### Abstract

There has been an increase in consumer demand for healthy food products made from natural ingredients. This demand has been partly addressed by the substitution of natural alternatives to synthetic ingredients. One such example in this endeavour, is the study of the application of natural biopolymers as food emulsion stabilisers. When biopolymers such as proteins and polysaccharides or their complexes are applied as emulsion stabilisers, they exhibit different modes of action. These include acting as emulsifiers (polypeptides), increasing the viscosity of the medium (polysaccharides), reducing coalescence by coating individual droplets as well as acting as weighting agents (polysaccharides and polypeptides). Biopolymers can be covalently complexed using chemical, enzymatic or thermal treatments. These treatments generally increase the robustness and solubility of the final complexes. Biopolymer complexes have been reported to show higher stability to varying temperatures, pH and ionic strength. When two incompatible biopolymers are mixed, either associative or segregative phase separation occurs. The former involves separation of oppositely charged polymers due to electrostatic repulsion and the latter involves separation of similarly charged or neutral biopolymers. In this chapter, the stabilising effect, complexation, mode of action, phase behaviour and future application of biopolymers in emulsions are discussed.

**Keywords:** biopolymers, polysaccharides, proteins, emulsion, stability, polysaccharide-protein complexes, phase-separation

# 1. Introduction

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Consumer demand for natural ingredients in food products has led to an upsurge of interest in the development of natural alternatives to synthetic ingredients. One avenue that has

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been explored is the employment of biopolymers as potential replacers of synthetic emulsion stabilisers. Biopolymers find technological application in many fields such as the food, microbiological, pharmaceutical and cosmetics industries. In many of these industries, the mostly used biopolymers are proteins and polysaccharides and are often applied in the production of colloidal dispersions such as foams or emulsions [1].

Biopolymers are long chain molecules composed of monomers covalently bonded together to form larger structures and can be divided into three groups, namely, polysaccharides, polypeptides and polynucleotides [1]. The scope of this review is limited to polysaccharides and polypeptides. Polysaccharides that have been studied include dietary fibre, starch, dextran, maltodextrin, pectin and carboxymethylcellulose [2]. Studies have shown that biopolymers can be employed as stabilisers on their own or in combination.

Although polymer-polymer complexes have been studied by various researchers [3–10], they still remain one of the most challenging topics to understand [9, 11]. These complexes are preferred in the food industry because of their sustainability, non-toxicity, non-immunogenicity, biocompatibility, good chemical reactivity, relatively low cost [12, 13], stability, nutritional benefits, biodegradability [14] as well as their generally-recognised-as-safe (GRAS) status. Furthermore, the replacement of synthetic stabilisers with natural biopolymers gives the product a 'clean' label.

Biopolymers are inherently present in food systems and they play a major role in food structure and stability [15]. In emulsions, they exhibit various modes of action including increasing the viscosity of the continuous phase thus retarding droplet movement [16], forming a fine film coating around individual oil droplets thereby reducing coalescence or increasing the oil droplet density, bringing it as close as possible to that of the aqueous phase, thereby reducing the rate of creaming. All these mechanisms increase the stability of emulsion systems and prolong the shelf life of the product.

Before a biopolymer hybrid can be applied as a stabiliser, it is of utmost interest to understand the interaction between the individual polymers, their phase behaviours as well as their interaction with the system. An understanding of the science behind the phase behaviour of a biopolymer system helps the formulator in designing and controlling the microstructure of the product [17]. Furthermore, since the phase morphology and interactions in polymeric mixtures largely influence the technological and functional properties of materials, having this knowledge beforehand is vital in predicting the behaviour of the product during processing, handling and distribution [18–19].

The main objective of this chapter is to highlight the importance, application, mode of action, phase behaviour and interaction of biopolymers (polysaccharides and proteins) in emulsion systems. This chapter also looks into the complexing mechanisms and phase separation of these biopolymers as well as details biopolymers that have been applied in food emulsions systems.

# 2. Emulsions and emulsion stability

An emulsion is a colloid that consists of two immiscible liquids, usually oil and water, with one of the liquids dispersed in the other [8, 20]. Emulsions consist of two phases; a dispersed

and a continuous phase, with the former consisting of the particles that make up the droplets and the latter being the surrounding liquid in which the droplets are dispersed in [20]. They can be categorised according to the relative spatial distribution of the oil and aqueous phase, the nature of the emulsifying agent or the arrangement of the system as shown in **Table 1**.

Examples of types of emulsions include oil-in-water (O/W), water-in-oil (W/O), macro-emulsions, micro-emulsions, bilayer droplets, multiple emulsions, mixed emulsions, pickering emulsions and glassy emulsions [8, 21–23]. The most common emulsions are oil-in-water and water-in-oil emulsions, with O/W emulsions being more popular that W/O emulsions [24]. Many food products such as butter (water-in-oil), margarine (oil-in-water), mayon-naise (O/W), salad dressings (O/W), vinaigrettes (O/W), homogenised milk (O/W), beverages (O/W) and ice cream (O/W) consist partly or fully of emulsions [25]. Emulsions can be further classified according to droplet size into three categories, namely, conventional emulsions (d < 200 nm), microemulsions (d < 100 nm) and nanoemulsions (d < 200 nm) [26, 27].

Emulsions are thermodynamically unstable systems and rapidly separate into separate layers of oil and water [21]. This is due to different densities between the oil and aqueous phases and the unfavourable contact between oil and water molecules [16, 28]. The stability of an emulsion can be defined as its ability to maintain their properties; that is the capability of the phases of the emulsion to remain mixed together [28]. The extent of emulsion stability is determined by various factors such as particle size, particle size distribution, density between the dispersed and continuous phases as well as the chemical integrity of the dispersed phase [26].

Several phenomena such as flocculation, coalescence, sedimentation, Ostwald ripening, creaming and phase inversion are responsible for the destabilisation of emulsions [29] as illustrated on **Figure 1**. Flocculation is the process where droplets in an emulsion are attracted to each other and form flocs without the rupture of the stabilising layer at the interface [30]. Droplet flocculation occurs due to gravitational force, centrifugation, Brownian forces as well as when the repulsive energy is less than van der Waals energy [31]. This phenomenon is undesirable as it promotes creaming and reduces clouding due to larger particle sizes, as well as promotes coalescence due to droplets being brought closer together [32].

| Nature of emulsifier                | System organisation        | Source |
|-------------------------------------|----------------------------|--------|
| Non-ionic surfactants               | Oil-in-water, water-in-oil | [21]   |
| Ionic surfactants                   | Macro-emulsions            | [29]   |
| Mixture of surfactants              | Micro-emulsions            | [4]    |
| Non-ionic polymers                  | Bilayer droplets           | [30]   |
| Polyelectrolytes                    | Multiple emulsions         | [23]   |
| Mixture of polymers and surfactants | Mixed emulsions            | [29]   |
| Solid particles                     | Pickering emulsion         | [22]   |
| Liquid crystalline phases           | Glassy emulsion            | [22]   |

Table 1. Classification of different types of emulsion.

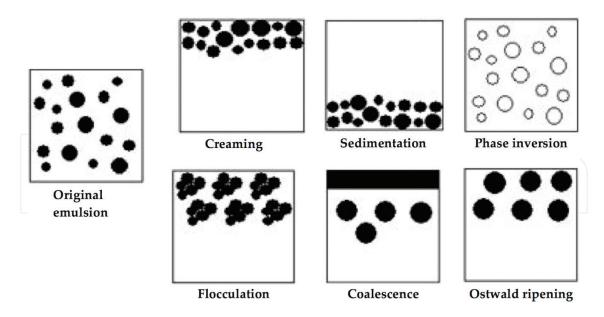


Figure 1. Mechanisms of emulsion destabilisation. Source: [36].

Creaming (upward) and sedimentation (downward) occur as a consequence of gravitational separation [30]. These occur when emulsion droplets merge together forming bigger droplets or when the droplets rise to the surface of the emulsion due to buoyancy. This is usually a result of gravitational force, when the density of the dispersed phase is less that the density of the continuous phase [33]. This phenomenon usually results in a separated emulsion with a droplet-rich cream layer and a droplet depleted watery layer [30]. Creaming is usually a precursor of coalescence and is followed by phase separation and its extent in O/W emulsions can be described using the creaming index. The creaming index gives insight into the extent of droplet aggregation that has occurred, as such, the higher the index, the more droplets have agglomerated [34]. Creaming can be measured by visual observation or by optical imaging.

Coalescence is the process where droplets come into contact and merge, creating larger droplets. With time, this reduces the average droplet size and consequently, reduces the stability of the emulsion. Ostwald ripening is a phenomenon where larger droplets expand at the expense of smaller ones and is largely affected by the solubility of the dispersed phase in the continuous phase [35].

These mechanisms of destabilisation occur due to several factors such as the nature and concentration of emulsifier or stabiliser, pH of the system, ionic strength, temperature, homogenisation parameters and interaction of dispersed with continuous phase [36, 37]. As such, substances such as emulsifiers, stabilisers, weighting agents, ripening inhibitors and texture modifiers (thickeners and gelling agents) are introduced to increase the kinetic stability of emulsion systems for longer periods of time [16, 31].

To produce a fine emulsion, large droplets are broken down into smaller ones by the application of intense mechanical energy [2]. For food emulsions, this is commonly accomplished using high-speed mixers, colloid mills or high-pressure valve homogenizers [2]. From a thermodynamic level, the emulsification process is very inefficient as most of the energy applied is dissipated as heat. The final droplet size of an emulsion is largely determined by the time taken to cover the interface with the emulsifier [5]. A slow emulsification rate results in the small droplets formed during emulsification, coalescing or flocculating.

# 3. Biopolymers as emulsion stabilisers

To increase the kinetic stability of emulsions, stabilisers such as emulsifiers, weighting agents, ripening inhibitors and texture modifiers (thickeners and gelling agents) are often used [16]. Stabilisers are a group of additives that are capable of stabilising emulsions by thickening the aqueous phase while emulsifiers are surface active molecules that adsorb to the surface of freshly formed droplets of an oil-water interface during homogenisation, forming a protective membrane that prevents the droplets from aggregating [2, 38]. As such, emulsifiers act as surface-modifying substances at the interface between each droplet and the continuous phase [20]. They are amphiphilic in nature, possessing both hydrophilic portions that align with the aqueous phase and hydrophobic portions that align with the lipid phase [39]. In this manner, they act as surface-modifying substances at the interface between each droplet and the continuous phase [20]. Emulsifiers can be oil or water soluble, forming a fluid, close-packed layer at the interface with a low interfacial tension. This results in an emulsion with a small droplet size distribution, stabilised by the fluid Gibbs-Marangoni mechanism or weak electrostatic repulsion [20].

Biopolymers such as polysaccharides and proteins are widely employed as functional ingredients in emulsion systems [9]. Most biopolymers have the ability to stabilise emulsions, but only a few possess emulsifying properties [10]. Being an emulsifier requires extensive surface activity at the oil-water interface, which is absent in most biopolymers such as polysaccharides [2]. The most commonly used emulsifier polysaccharides in food include gum Arabic, modified starch, modified cellulose, pectin and galactomannans [39–41]. The effectiveness of biopolymers as emulsifiers is highly dependent on factors such as concentration and rate of adsorption [42]. At low concentrations, the biopolymer may fail to cover the entire surface of droplets, resulting in coalescence and consequent destabilisation [43].

Polysaccharides that have been studied include dietary fibre, starch, dextran, maltodextrin, pectin, carboxymethylcellulose (CMC) as well as many other gums [2]. They stabilise emulsions either by modification of the rheological properties of the bulk phase or adsorption at the oil-water interface, thereby providing a steric or an electrosteric barrier, or a combination of the two effects. They reduce the interfacial tension and thus the amount of work that is necessary to create new surfaces and they enhance the formation of small droplets and diminish the rate at which droplets [44]. Proteins on the other hand, have been reported to stabilise emulsions by forming a viscoelastic, adsorbed layer on the oil droplets, which forms a physical barrier, hindering the contact of droplets, thus reducing coalescence and flocculation [20, 45].

# 4. Polysaccharide-protein conjugates in emulsions

There is growing interest in harvesting the combined beneficial attributes of protein and polysaccharides as emulsifiers and stabilisers through the production of polysaccharide-protein conjugates [2, 44]. Many emulsions constitute of polysaccharide-protein combinations [46]. These biopolymers are excellent ingredients in food emulsions as they alter the rheological characteristics of the system through their gelling networking system [36]. As such, vastly increase emulsion stability by reducing surface tension and retarding droplet movement in the thicker aqueous phase [47].

Proteins are able to adsorb on droplet surfaces, thus decreasing interfacial tension and enhancing interfacial elasticity [48], therefore, they interact through electrostatic or hydro-phobic-hydrophobic interactions [9], while polysaccharides being hydrophilic in nature, tend to remain dispersed within the aqueous phase, increasing thickening and gelling. Although some polysaccharides are able to adsorb at a globule surface, most stabilise emulsions by increasing the viscosity of the continuous phase, thus impeding droplet movement [48].

As such, protein-polysaccharide complexes are excellent emulsifiers because of their combined hydrophilic and hydrophobic properties [15]. These biopolymer mixtures further increase emulsion stability due to cooperative adsorption of protein and polysaccharide at the emulsion droplet interface [15]. Some protein-polysaccharide conjugates that have been studied as emulsion stabilisers are given in **Table 2**.

Proteins and polysaccharides are capable of forming associations through covalent bonds between the reducing end of the polysaccharide and the lysine amino group of the protein, as well as non-covalent interactions such as electrostatic interactions, hydrophobic interactions,

| Polysaccharide                 | Protein               | Source |
|--------------------------------|-----------------------|--------|
| Dextran                        | Soybean protein       | [48]   |
| Soybean soluble polysaccharide | Pea protein           | [14]   |
| Dextran                        | Whey protein          | [2]    |
| Carboxymethylcellulose         | Egg yolk protein      | [41]   |
| Pectin                         | Whey protein          | [2]    |
| Gum Arabic-                    | Flaxseed protein      | [49]   |
| Pectin                         | Pea protein           | [50]   |
| Soybean polysaccharide         | Pea protein           | [14]   |
| Gum Arabic                     | Flaxseed protein      | [51]   |
| Dextran                        | Whey protein          | [52]   |
| Ovalbumin                      | Caboxymethylcellulose | [17]   |
| Whey protein                   | Wheat starch          | [18]   |
| Whey protein                   | Xanthan               | [53]   |
| Gelatin                        | Pectin                | [53]   |
| Gelatin                        | Starch                | [53]   |

Table 2. Protein-polysaccharide complexes previously studied.

hydrogen bonding,  $\pi$ - $\pi$  stacking, co-ordinating forces and van der Waals [49]. These bonding mechanisms allow polysaccharide-protein complexes to alter the interfacial behaviour and consequently, the stability of the emulsions [5]. The combination of the properties of these biopolymers under appropriate conditions leads to increased emulsion stability [48]. **Figure 2** shows a representation of the possible mode of interaction between polysaccharides and proteins.

The polysaccharide-protein complex has improved attributes than each polymer on its own. The presence of bound protein renders the complex more surface active than the biopolymer on its own; enabling it to achieve surface layer saturation at a significantly lower concentration [2]. Also, because of the covalently bound polysaccharide, the protein adsorbed at the interfacial layer is protected against destabilisation under undesirable conditions [5].

Polysaccharides such as xanthan, when used in emulsion systems, control texture and stability, influence pseudoplastic flow at low concentrations and retard the rate of creaming and/or sedimentation of particles under inert or low shear conditions yet allow production processes

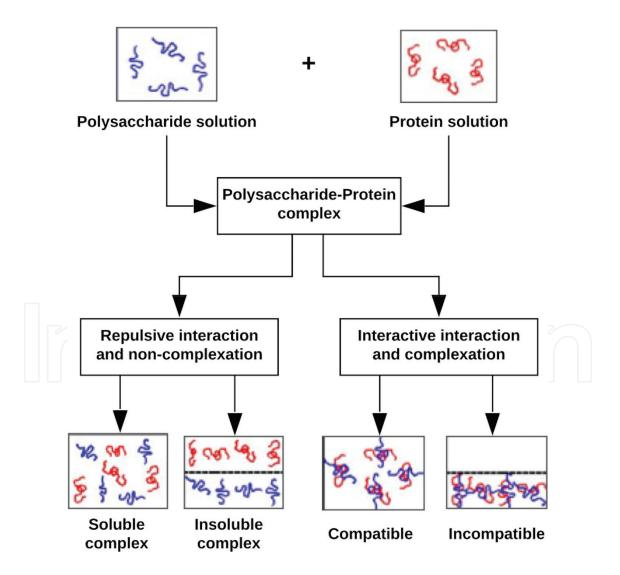


Figure 2. Representation of the possible mode of interaction between polysaccharides and proteins.

such as pumping and filling under high shear [19]. When used in combination with a protein, xanthan stabilises emulsions as an indirect consequence of depletion flocculation, resulting in a mechanically stable protein and droplet rich network surrounded by a xanthan-rich phase [19].

# 5. Biopolymer complexation and phase behaviour

The covalent linkage of polysaccharide to protein can be obtained using chemical [51], enzymatic [52] or thermal treatments [53]. Thermal treatment is the most commonly used of the techniques and involves exposing a dry mixture of the protein and polysaccharide to heat [53]. This heat induced complexing has been reported to improve protein solubility and stability under undesirable medium conditions such as high temperatures, low pH and high ionic strength [53].

The thermal complexation of polysaccharide to protein or protein to protein can be carried out in a two-step process. The first step involves the application of heat which denatures the protein and results in the unfolding of the chain, exposing sulphhydryl and hydrophobic groups. This then allows the protein to form sulphhydryl groups with other chains and hydrophobic interactions with polysaccharides. The second stage involves the aggregation of the biopolymers through covalent and non-covalent interactions, giving the final complex [54]. When dry heating is applied, the protein and polysaccharide form Maillard-type conjugates. This treatment improves the solubility of the protein, the stability of the emulsion as well as improves the interfacial functionality of the protein [1].

Polysaccharide-protein conjugate stabilised emulsions can be obtained using the mixed-emulsion or bilayer-emulsion approaches. In the former, an aqueous solution containing the polysaccharide-protein complex is added to an emulsion, following homogenisation. In the latter, a charged polysaccharide solution is added to an emulsion system that is stabilised by proteins, thereby forming an emulsion with a polysaccharide-protein 'bilayer' surface coating [9]. The mixed-emulsion approach produces more stable emulsions while the bi-layer approach has a tendency to lead to extensive flocculation during preparation. In the bilayer methodology, the concentration of the polysaccharide needs to be carefully controlled. If a polysaccharide is present in low concentrations, the viscosity of the medium remains low therefore allowing for bridging flocculation to occur as droplet collision will occur at a faster rate than polysaccharide saturation. If a polysaccharide is present in high concentrations, then unadsorbed polysaccharide exceed a certain critical value resulting in depletion flocculation [49].

The complexing of proteins and polysaccharides can be summarised as a two stage process, highly dependent on the pH of the medium [15]. The first stage involves the formation of intramolecular soluble complexes and the second stage involves the formation of intermolecular complexes. In the second stage, insoluble complexes can be formed. The formation of insoluble complexes can lead to liquid-liquid phase separation (coacervation) or precipitation, depending on the charge density of the polysaccharide [15].

Mixtures of proteins and polysaccharides in aqueous media influence the phase behaviour of the system, influencing the overall structural and textural properties, and ultimately their stability [55].

Such mixtures display one of three equilibrium states, namely, miscibility, complex coacervation or thermodynamic incompatibility [17]. Miscibility occurs when the two biopolymers are co-soluble and are compatible [55]. Complex coacervation and thermodynamic incompatibility occur at high biopolymer concentration and the former occurs when the net attraction between the biopolymers is attractive while the latter occurs when the net charge is repulsive [17].

There are five stages of structural transition involved in the formation of a protein-polysaccharide complex [15]. These are: (1) stable region of mixed individual soluble polymers; (2) stable region of intramolecular soluble complexes; (3) a partially stable region of intermolecular soluble complexes; (4) an unstable region of intermolecular insoluble complexes; and (5) a second stable region of mixed individual soluble polymers. Intermolecular forces are formed between proteins and anionic polysaccharides when these biopolymers carry opposite charges and occur more efficiently when the pH is below the Isoelectric point (pI) of the protein [55]. Complex formation is constrained at high ionic strengths and when the pH of the medium is above the pI of the protein. A mixture of protein and polysaccharides exhibits different phase behaviours with synergistic or antagonistic action, resulting in soluble and insoluble complexes, respectively [15].

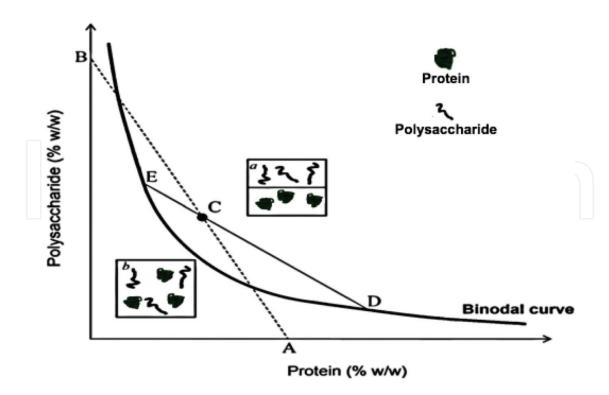
#### 5.1. Phase separation mechanisms

Phase separation is a phenomenon where biopolymer mixtures are thermodynamically incompatible and therefore separate into distinct phases [17, 19]. If proteins and polysaccharides in mixtures are incompatible, then protein-polysaccharide coacervation or phase separation into a protein-rich phase or polysaccharide-rich phase, occurs [19]. Initial phase separation in biopolymer systems results in one phase staying continuous while the other remains dispersed through it as small liquid droplets [54]. When mixtures of proteins and polysaccharides above the minimum critical gelling concentration are subjected to thermal treatment, they exhibit micro-phase separation networks. This occurs when no overriding drive to heterotypic binding prevails [18]. In this instance, one polymer forms the continuous phase and the other remains contained in the form of discontinuous inclusions [18].

Phase separation is dependent on medium conditions such as pH, ionic strength as well as nature and concentration of biopolymers [19]. At equilibrium, the protein-polysaccharide mixture separates into a protein-rich lower phase and a polysaccharide-rich upper phase [55]. An accumulation of colloidal particles at the water-water interface of a starch-gelatin system was observed and this behaviour was reported to change the nature of the microstructure and dynamics of phase separation of the system [19].

If two biopolymers are used in an emulsion system but do not interact with each other, they exist either in a single-phase system or in a phase separated system [10]. In a single-phase system, the two biopolymers exist separately, distributed throughout the medium, while in a phase separated system, the biopolymers exist as two distinct phases. Phase separation can be associative or segregative [56–58].

The phase separation of protein-polysaccharide mixtures can be quantitatively described using phase diagrams, such as the binodal curve (**Figure 3**). The binodal curve separates the



**Figure 3.** Phase separation diagram of a protein-polysaccharide mixture adapted from: [1]. **A**: protein; **B**: polysaccharide; **C**: initial mixture of protein and polysaccharide; **D**: composition of protein-rich phase; **E**: composition of polysaccharide-rich phase; **a**: distinct separation of phases; and **b**: biopolymers co-existing but mutually excluding each other.

region of co-solubility from that of phase separation. The separation of the mixture occurs above a certain critical concentration (represented by the binodal curve in **Figure 3**), below which the biopolymers co-exist in a single phase and above which a distinct separation into protein-rich and polysaccharide-rich phases is observed [1].

#### 5.1.1. Associative phase separation

Associative phase separation occurs if the two polymers are oppositely charged, such as an ionic polysaccharide and a protein, leading to electrostatic attraction and consequently resulting in separation into two clear coacervate/precipitate and supernatant phases [15, 59]. Essentially, associative phase separation involves the formation of two distinct phases, one very rich in both biopolymers and the other with very small amounts of the biopolymers. The biopolymer rich phase is formed when the soluble biopolymer complexes interact and form neutral aggregates which eventually sediment and form a precipitate [1]. Associative phase separation can be reversible or irreversible, depending on the strength of bonds formed. In complexes where the polysaccharide is negatively charged and the protein is positively charged, strong electrostatic complexes are formed which may be irreversible. Reversible complexes are formed between negatively charged polysaccharides and a negatively charged protein or a protein carrying nearly a zero charge (pH  $\approx$  pI).

#### 5.1.2. Segregative phase separation

Segregative phase separation occurs between two biopolymers carrying a similar charge, two neutral biopolymers or one charged biopolymer and a neutral biopolymer. This leads to

electrostatic repulsion or steric exclusion, resulting in mutual exclusion of each polymer from the vicinity of the other and consequently resulting in the two biopolymers separating into two distinct phases [58]. This separation mechanism is commonly observed in semi-dilute or concentrated mixed emulsions [1]. An example of a system that would undergo segregative phase separation is that consisting of gum Arabic and sugar beet pectin. Both hydrocolloids are negatively charged and would therefore repel each other, resulting in separation into two layers [15].

An advantage of phase separation could be its potential in producing functional components. Molecular fractionation of gum Arabic when complexed with protein has been previously reported [30]. As the extent of phase separation increased, the amount of arabinogalactan-protein complex increased by more than twice in the gum Arabic rich phase. The researchers hypothesised that phase separation was responsible for the molecular fractionation and could therefore be used to obtain purified functional components from polydisperse hydrocolloids.

#### 5.2. Factors affecting the stability of emulsions stabilised by biopolymers

The solubility and behaviour of biopolymers is dependent on various factors, such as pH, ionic strength, temperature, nature of biopolymers and medium, presence of other agents such as surfactants in the system and charge of biopolymers [10, 41]. When proteins and polysaccharides coexist in an emulsion system, the pH of that system determines the ability of these biopolymers to maintain its stability. When the pH of the emulsion medium is lower than the pI of the protein, the net positive charge of the protein interacts with the negative charge of polysaccharides [59]. Likewise, if the pH is above the pI, then the net negative charge of the proteins interacts with the positive charges of polysaccharides [2]. When the pH is equal or almost equal to the pI of the protein, then the net charge of the protein will be zero, making it unable to form any interactions [10].

The interaction of proteins and polysaccharides as well as the effectiveness of the polysaccharide-protein complexes as emulsion stabilisers, are greatly influenced by factors such as nature of the polysaccharide or protein, charge density, hydrophobicity or hydrophilicity, charge density and molecular weight [9].

# 6. Future prospects

Future studies could look into the use of polysaccharide-polysaccharide and polysaccharideprotein complexes as delivery vehicles for nutrients and bioactive compounds in food products. Studies into the nanoencapsulation of therapeutic metabolites using biopolymers as encapsulating agents should also be considered. Studies would then look into the physicochemical properties of these biopolymer and biopolymer complexes as well as their interaction with various emulsion media. Furthermore, biopolymers from lesser crops and climate smart crops such as Bambara groundnut, pigeon pea, yam bean, morama bean and grass pea need to be investigated. Studies have looked into the application of polysaccharides from Bambara groundnut as emulsion stabilisers and emulsifiers [28, 60–63]. These researchers reported that high concentrations of polysaccharide were required to attain a desirable stability within the studied emulsions. Complexing polysaccharides from lesser legumes with proteins would ensure the use of lower concentrations of polysaccharides while attaining robust complexes with emulsifying and stabilising properties. Furthermore, lesser crops thrive in adverse weather conditions and are nutritionally rich, making them suitable alternatives, in the face of global climate changes. Proteins such as those of pea origin can also be used as alternatives to widely utilised proteins such as soy protein.

# 7. Conclusions

In conclusion, biopolymers play a significant role in emulsion stabilisation and have a huge potential of replacing synthetic stabilisers in food emulsions, thus allowing the development of products with 'clean' labels. Polysaccharides alter the viscosity of the aqueous phase, forming a gel network that impedes droplet migration while proteins on the other hand, are surface active hence possess emulsifying capabilities. As such, the application of polysaccharides in combination with proteins, in emulsion systems, results in improved stabilising properties at lower concentrations. The biopolymer concentration, mechanism of complexing, nature of system and systems' intrinsic factors need to be carefully considered when preparing biopolymer stabilised emulsions to allow compatibility and hence long-term stability. Furthermore, the inclusion of biopolymers in emulsions not only increases their stability but also positively impact the nutritional value, shelf life, texture and mouthfeel of the final product.

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# References

- [1] Mohan S, Oluwafemi OS, Kalarikkal N, Thomas S, Songca SP. Biopolymers-application in nanoscience and nanotechnology. In: Perveen FK, editor. Recent Advances in Biopolymers. Croatia: InTech; 2016. pp. 47-72. DOI: 10.5772/52807
- [2] Dickinson E. Hydrocolloids as emulsifiers and emulsion stabilizers. Food Hydrocolloids. 2009;**23**(6):1473-1482. DOI: 10.1016/j.foodhyd.2008.08.005
- [3] Bos MA, Van Vliet T. Interfacial rheological properties of adsorbed protein layers and surfactants: A review. Advances in Colloid and Interface Science. 2001;91:437-471. DOI: 10.1016/S0001-8686(00)00077-4

- [4] Benichou A, Aserin A, Garti N. Double emulsions stabilized by new molecular recognition hybrids of natural polymers. Polymers for Advanced Technologies. 2002;13(10-12):1019-1031. [cited 2017 Oct 27]. Available from: http://doi.wiley.com/10.1002/pat.270. DOI: 10.1002/pat.270
- [5] Dickinson E. Hydrocolloids at interfaces and the influence on the properties of dispersed systems. Food Hydrocolloids. 2003;17:25-39. DOI: 10.1016/S0268-005X(01)00120-5
- [6] Mackie AR. Structure of adsorbed layers of mixtures of proteins and surfactants. Current Opinion in Colloid & Interface Science. 2004;9:357-361. DOI: 10.1016/j.cocis.2004.08.001
- [7] Sánchez CC, Patino JMR. Interfacial, foaming and emulsifying characteristics of sodium caseinate as influenced by protein concentration in solution. Food Hydrocolloids. 2005;19(3):407-416. DOI: 10.1016/j.foodhyd.2004.10.007
- [8] McClements DJ, Decker EA, Weiss J. Emulsion-based delivery systems for lipophilic bioactive components. Journal of Food Science. 2007;72(8). DOI: 10.1111/j.1750-3841. 2007.00507.x
- [9] Bandyopadhyay P, Ghosh AK, Ghosh C. Recent developments on polyphenol–protein interactions: Effects on tea and coffee taste, antioxidant properties and the digestive system. Food & Function. 2012;3(6):592. DOI: 10.1039/c2fo00006g
- [10] Evans M, Ratcliffe I, Williams PA. Emulsion stabilisation using polysaccharide-protein complexes. Current Opinion in Colloid & Interface Science. 2013;18:272-282. DOI: 10.1016/j.cocis.2013.04.004
- [11] Doublier JL, Garnier C, Renard D, Sanchez C. Protein-polysaccharide interactions. Current Opinion in Colloid & Interface Science. 2000;5:202-214. DOI: 10.1016/S1359-0294(00)00054-6
- [12] Spizzirri UG, Parisi OI, Iemma F, Cirillo G, Puoci F, Curcio M, et al. Antioxidantpolysaccharide conjugates for food application by eco-friendly grafting procedure. Carbohydrate Polymers. 2010;79(2):333-340. DOI: 10.1016/j.carbpol.2009.08.010
- [13] Song WL, Wang P, Cao L, Anderson A, Meziani MJ, Farr AJ, et al. Polymer/boron nitride nanocomposite materials for superior thermal transport performance. Angewandte Chemie, International Edition. 2012;51(26):6498-6501. DOI: 10.1002/anie.201201689
- [14] Yin B, Zhang R, Yao P. Influence of pea protein aggregates on the structure and stability of pea protein/soybean polysaccharide complex emulsions. Molecules. 2015;20(3):5165-5183. DOI: 10.3390/molecules20035165
- [15] Gao Z, Fang Y, Cao Y, Liao H, Nishinari K, Phillips GO. Hydrocolloid-food component interactions. Food Hydrocolloids. 2017;68:149-156. DOI: 10.1016/j.foodhyd.2016.08.042
- [16] Kerkhofs S, Lipkens H, Velghe F, Verlooy P, Martens JA. Mayonnaise production in batch and continuous process exploiting magnetohydrodynamic force. Journal of Food Engineering. 2011;106(1):35-39. DOI: 10.1016/j.jfoodeng.2011.04.003

- [17] Jia W, Cui B, Ye T, Lin L, Zheng H, Yan X, et al. Phase behavior of ovalbumin and carboxymethylcellulose composite system. Carbohydrate Polymers. 2014;109:64-70. DOI: 10.1016/j.carbpol.2014.03.026
- [18] Yang N, Liu Y, Ashton J, Gorczyca E, Kasapis S. Phase behaviour and in vitro hydrolysis of wheat starch in mixture with whey protein. Food Chemistry. 2013;137(1-4):76-82.
  DOI: 10.1016/j.foodchem.2012.10.004
- [19] Hanazawa T, Murray BS. The influence of oil droplets on the phase separation of proteinepolysaccharide mixtures. Food Hydrocolloids. 2014;34:128-137. Available from: http://ac.els-cdn.com/S0268005X12002901/1-s2.0-S0268005X12002901-main.pdf?\_ tid=790b45d6-9e19-11e7-bbcf-00000aab0f27&acdnat=1505921971\_24b3487078673f13ce99 22a2cdbf89a2. DOI: 10.1016/j.foodhyd.2012.11.025
- [20] Robins MM, Watson AD, Wilde PJ. Emulsions Creaming and rheology. Current Opinion in Colloid & Interface Science. 2002;7(5-6):419-425. DOI: 10.1016/S1359-0294(02)00089-4
- [21] Ghosh S, Rousseau D. Fat crystals and water-in-oil emulsion stability. Current Opinion in Colloid and Interface Science. 2011;**16**:421-431. DOI: 10.1016/j.cocis.2011.06.006
- [22] Tadros TF. Emulsion Formation, Stability, and rheology. In: Emulsion Formation and Stability. Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA; 2013. pp. 1-76. DOI: 10.1002/9783527647941.ch1
- [23] Singh VK, Kumar D. Effect of fibres on properties of concrete. International Journal of Computer and Mathematical Sciences. 2014;**3**(6):111-119
- [24] Williams PA. Food emulsions: Principles, practice, and techniques. International Journal of Food Science and Technology. 2001;36(2):223-224. Available from: DOI: http://doi. wiley.com/10.1046/j.1365-2621.2001.00459.x, 10.1046/j.1365-2621.2001.00459.x
- [25] Piorkowski DT, McClements DJ. Beverage emulsions: Recent developments in formulation, production, and applications. Food Hydrocolloids. 2014;42:5-41. DOI: 10.1016/j. foodhyd.2013.07.009
- [26] Given PS. Encapsulation of flavors in emulsions for beverages. Current Opinion in Colloid & Interface Science. 2009;14:43-47. DOI: 10.1016/j.cocis.2008.01.007
- [27] Zhang R, McClements DJ. Enhancing nutraceutical bioavailability by controlling the composition and structure of gastrointestinal contents: Emulsion-based delivery and excipient systems. Food Structure. 2016;10:21-36. DOI: 10.1016/j.foostr.2016.07.006
- [28] Maphosa Y, Jideani VA, Adeyi O. Effect of soluble dietary fibres from Bambara groundnut varieties on the stability of orange oil beverage emulsion. African Journal of Science, Technology, Innovation and Development. 2017;9(1):69-76. DOI: 10.1080/20421338.2016. 1263436
- [29] Zhang J, Gao Y, Qian S, Liu X, Zu H. Physicochemical and pharmacokinetic characterization of a spray-dried malotilate emulsion. International Journal of Pharmaceutics. 2011;414(1-2):186-192. DOI: 10.1016/j.ijpharm.2011.05.032

- [30] Mao L, Miao S. Structuring food emulsions to improve nutrient delivery during digestion. Food Engineering Reviews. 2015;7:439-451. DOI: 10.1007/s12393-015-9108-0
- [31] Payet L, Terentjev EM. Emulsification and stabilization mechanisms of O/W emulsions in the presence of chitosan. Langmuir. 2008;**24**(21):12247-12252. DOI: 10.1021/la8019217
- [32] Chanamai R, McClements DJ. Impact of weighting agents and sucrose on gravitational separation of beverage emulsions. Journal of Agricultural and Food Chemistry. 2000;48(11):5561-5565. DOI: 10.1021/jf0002903
- [33] Tadros T. Application of rheology for assessment and prediction of the long-term physical stability of emulsions. Advances in Colloid and Interface Science. 2004;108-109:227-258. DOI: 10.1016/j.cis.2003.10.025
- [34] Onsaard E, Vittayanont M, Srigam S, McClements DJ. Comparison of properties of oil-in-water emulsions stabilized by coconut cream proteins with those stabilized by whey protein isolate. Food Research International. 2006;39(1):78-86. DOI: 10.1016/j. foodres.2005.06.003
- [35] Jiao J, Burgess DJ. Ostwald ripening of water-in-hydrocarbon emulsions. Journal of Colloid and Interface Science. 2003;264(2):509-516. DOI: 10.1016/S0021-9797(03)00276-5
- [36] McClements DJ. Food Emulsions Principles, Practices, and Techniques. 2nd ed2005. DOI: 10.1093/acprof:oso/9780195383607.003.0002
- [37] Sjöblom J. Emulsion and Emulsion Stability. 2006. pp. 185-223. DOI: 10.1016/0300-9572(85)90015-2
- [38] Weiss J. Emulsion stability determination. In: Wrolstad RE, editor. Handbook of Food Analytical Chemistry. New Jersey: John Wiley & Sons Inc.; 2005. pp. 591-607. DOI: 10.1002/ 0471709085.part5
- [39] Cottrell T, Van Peij J. Emulsifiers in Food Technology [Internet]. 2nd ed. Emulsifiers in Food Technology; 2014. pp. 73-92 p. Available from: http://www.scopus.com/inward/record.
  url?eid=2-s2.0-84926136393&partnerID=tZOtx3y1DOI. DOI: 10.1002/9781118921265.ch4
- [40] Castellani O, Guibert D, Al-Assaf S, Axelos M, Phillips GO, Anton M. Hydrocolloids with emulsifying capacity. Part 1 - emulsifying properties and interfacial characteristics of conventional (*Acacia senegal* (L.) Willd. Var. senegal) and matured (Acacia (sen) SUPER GUMTM) Acacia Senegal. Food Hydrocolloids. 2010;24(2-3):193-199. DOI: 10.1016/j.foodhyd.2009.09.005
- [41] Lim SS, Baik MY, Decker EA, Henson L, Michael Popplewell L, McClements DJ, Choi SJ. Stabilization of orange oil-in-water emulsions: A new role for ester gum as an Ostwald ripening inhibitor. Food Chemistry. 2011;128(4):1023-1028. DOI: 10.1016/j.foodchem. 2011.04.008
- [42] de Souza CJF, Rojas EEG. Emulsion of systems containing egg yolk, polysaccharides and vegetable oil. Ciencia E Agrotecnologia. 2012;36(5):543-550. DOI: 10.1590/S1413-70542012000500007

- [43] Zhao X, Liu F, Ma C, Yuan F, Gao Y. Effect of carrier oils on the physicochemical properties of orange oil beverage emulsions. Food Research International. 2015;74:260-268. DOI: 10.1016/j.foodres.2015.05.002
- [44] Koocheki A, Ghandi A, Razavi SMA, Mortazavi SA, Vasiljevic T. The rheological properties of ketchup as a function of different hydrocolloids and temperature. International Journal of Food Science and Technology. 2009;44(3):596-602. DOI: 10.1111/j.1365-2621.2008.01868.x
- [45] Guzey D, McClements DJ. Formation, stability and properties of multilayer emulsions for application in the food industry. Advances in Colloid and Interface Science. 2006;128-130:227-248. DOI: 10.1016/j.cis.2006.11.021
- [46] Ron EZ, Rosenberg E. Biosurfactants and oil bioremediation. Current Opinion in Biotechnology. 2002;13:249-252. DOI: 10.1016/S0958-1669(02)00316-6
- [47] Rodriguez Patino JM, Pilosof AMR. Protein-polysaccharide interactions at fluid interfaces. Food Hydrocolloids. 2011;25(8):1925-1937. DOI: 10.1016/j.foodhyd.2011.02.023
- [48] Bouyer E, Mekhloufi G, Rosilio V, Grossiord JL, Agnely F. Proteins, polysaccharides, and their complexes used as stabilizers for emulsions: Alternatives to synthetic surfactants in the pharmaceutical field? International Journal of Pharmaceutics. 2012;436:359-378. DOI: 10.1016/j.ijpharm.2012.06.052
- [49] De Kruif CG, Tuinier R. Polysaccharide protein interactions. Food Hydrocolloids. 2001;15(4-6):555-563. DOI: 10.1016/S0268-005X(01)00076-5
- [50] Jiménez-Castaño L, Villamiel M, López-Fandiño R. Glycosylation of individual whey proteins by Maillard reaction using dextran of different molecular mass. Food Hydrocolloids. 2007;21(3):433-443. DOI: 10.1016/j.foodhyd.2006.05.006
- [51] Diftis NG, Biliaderis CG, Kiosseoglou VD. Rheological properties and stability of model salad dressing emulsions prepared with a dry-heated soybean protein isolate-dextran mixture. Food Hydrocolloids. 2005;19(6):1025-1031. DOI: 10.1016/j.foodhyd.2005.01.003
- [52] Flanagan J, Singh H. Recent Advances in the Delivery of Food-Derived Bioactives and Drugs Using Microemulsions. Nanocarrier Technologies: Frontiers of Nanotherapy; 2006. pp. 95-111. DOI: 10.1007/978-1-4020-5041-1\_7
- [53] Oliver CM, Melton LD, Stanley RA. Creating proteins with novel functionality via the maillard reaction: A review. Critical Reviews in Food Science and Nutrition. 2006;46(4):337-350. DOI: 10.1080/10408690590957250
- [54] Fitzsimons SM, Mulvihill DM, Morris ER. Segregative interactions between gelatin and polymerised whey protein. Food Hydrocolloids. 2008;22(3):485-491. DOI: 10.1016/j. foodhyd.2007.01.005
- [55] Mession JL, Assifaoui A, Lafarge C, Saurel R, Cayot P. Protein aggregation induced by phase separation in a pea proteins-sodium alginate-water ternary system. Food Hydrocolloids. 2012;28(2):333-343. DOI: 10.1016/j.foodhyd.2011.12.022

- [56] Tolstoguzov V. Phase behavior in mixed polysaccharide systems. In: Food Polysaccharides and Their Applications [Internet]; 2006. pp. 589-627. Available from: http://www.crcnetbase.com/doi/abs/10.1201/9781420015164.ch6%5Cnhttp://www.crcnetbase.com/doi/ abs/10.1201/9781420015164.ch17DOI: 10.1201/9781420015164.ch17
- [57] Fang Y, Li L, Inoue C, Lundin L, Appelqvist I. Associative and segregative phase separations of gelatin/??- carrageenan aqueous mixtures. Langmuir. 2006;22(23):9532-9537. DOI: 10.1021/la061865e
- [58] Jha PK, Desai PS, Li J, Larson RG. pH and salt effects on the associative phase separation of oppositely charged polyelectrolytes. Polymer. 2014;6(5):1414-1436. DOI: 10.3390/ polym6051414
- [59] Schmitt C, Turgeon S. Protein/polysaccharide complexes and coacervates in food systems. Advances in Colloid and Interface Science. 2010;**167**:63-70. DOI: 10.1016/j.cis.2010.10.001
- [60] Adeyi O, Ikhu-Omoregbe D, Jideani V. Emulsion stability and steady shear characteristics of concentrated oil-in-water emulsion stabilized by gelatinized bambara groundnut flour. Asian Journal of Chemistry. 2014;26:4995-5002. DOI: 10.14233/ajchem.2014.16287
- [61] Gabriel EG, Jideani VA, Ikhu-omoregbe DIO. Investigation of the emulsifying properties of Bambara groundnut flour and starch. International Journal of Food Science and Engineering. 2013;7(11):539-547





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